Journal of Industrial and Engineering Chemistry 33 (2016) 209–220

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Deep HOMO polymers comprising anthracene units for bulk heterojunction solar cells

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ARTICLE INFO

Article history:
Received 24 July 2015
Received in revised form 3 October 2015
Accepted 3 October 2015
Available online 30 October 2015

Keywords:
Anthracene
Benzooxadiazole
Benzothiadiazole
Side chain manipulation
Bulk heterojunction polymer solar cells

ABSTRACT

Four anthracene-based D–π–A polymers, poly[anthracene-*alt*-4,7-bis(thiophen-2-yl)-5,6-bis(octyloxy)benzo[*c*][1,2,5]thiadiazole] (P1, P3) and Poly[anthracene-*alt*-4,7-bis(thiophen-2-yl)-5,6-bis(octyloxy)benzo[*c*][1,2,5]oxadiazole] (P2, P4), were successfully polymerized through Suzuki coupling reaction. The polymers include benzooxaediazole (BO), PAnoBO, and PAnoBO-EH exhibited the deep HOMO level (−5.39 eV or lower) because BO has a lower lying oxidation potential than Benzothiadiazole (BT). BO acceptor enhanced the electron withdrawing property of the polymers, inducing long-wavelength absorption and 0.05–0.1 eV reduction in the band-gap. For solar cells using a PAnoBO:$PC_{71}BM$ (1:4, w/w), the resulting J_{sc}, Voc, FF, and PCE were 3.1 mA/cm^2, 0.74 V, 48.8%, and 1.2%, respectively.

Introduction

For several decades, polymer solar cells (PSCs) with a bulk heterojunction (BHJ) structure have received considerable attention. They have several advantages over traditional PV cells such as their low cost, low weight, applied over large surfaces and use a sustainable source of energy: sunlight. Therefore, many investigations into new organic semiconductors with superior photovoltaic properties have been carried out [1–4].

In general, the active layer of a high-efficiency PSC is composed of a blended bulk heterojunction (BHJ) configuration consisting of an electron-donor (conducting polymer) and an electron acceptor (a fullerene derivative) [5,6]. For BHJ solar cells, high efficiency can be achieved by designing and tuning the chemical and structural parameters of the donor polymer (e.g., the conjugated backbone and side chains). In particular, the donor–acceptor (D–A) concept has been widely used in the design of conjugated polymers that are used in PSCs [7,8]. Their molecular orbitals can be fine-tuned by a choice of donor and acceptor. The ideal conjugated polymer for PSCs must have both broad absorption and a high absorption coefficient in the visible and near-infrared regions. Moreover, it must have high hole mobility and suitable HOMO and LUMO energy levels. Also, to assemble the active layer, it should also be miscible with the fullerene component to generate the appropriate nano-structured film [9,10]. Recently, high efficiency has been achieved using a conjugated polymer formed of a backbone with alternating units of an electron-rich donor and an electron-deficient acceptor [11–14].

Various organic electronic devices have been built using anthracene-based polymers as the donor unit in D–A type polymers. In particular, for organic photovoltaics (OPVs), good charge transport properties have been achieved in these polymers because of the planarity and rigidity of anthracene. Furthermore, anthracene has a low HOMO energy level, resulting in a high open voltage current (V_{oc}). However, further optimization of its solubility is necessary to enable the use of solution processing [15,16]. In general, unsubstituted anthracene derivatives without side-chains are poorly soluble in organic solvents. Therefore, in this report, we describe out attempts to improve the solubility of the anthracene-copolymer by introducing bulky side chains at the 9- and 10-positions of anthracene. However, the introduction of side chains can reduce the charge transport properties and interrupt the intermolecular packing of the copolymer when formed into a thin film. Therefore, it is important to select an appropriate side chain and acceptor to synthesize a copolymer with both good solubility and good intermolecular packing [17,18]. Also, the donor unit of a D–A type polymer should be paired with acceptors that

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http://dx.doi.org/10.1016/j.jiec.2015.10.010
1226-086X/

lower the energy of the polymer LUMO. Benzothiadiazole (BT) has been widely used in PSCs as a strong electron-withdrawing unit. It is an electron-acceptor and has a quinoid structure, and these features can reduce the band-gap while allowing the formation of coplanar polymers [19–23]. Using benzoxadiazole (BO), which is a structure analog of BT, forms a polymer with lower HOMO and LUMO energy levels. In addition, polymers contain BO are air-stable. Moreover, when the polymer is blended with fullerene, high open-circuit voltages are achieved. However, in the case of several polymers based on BO, their low solubility led to the formation of low molecular weight polymers with low power conversion efficiencies (PCEs). Later, Wei et al. reported that the introduction of the octyloxy chain at the 5- and 6-positions of BO could improve polymer solubility [24–31].

In this report, we synthesized four D–A-type polymers, labeled P1, P2, P3, and P4, based on anthracene derivatives containing acceptors with different electron-withdrawing properties. The optical and electrochemical properties of BT and BO polymers are also described. We concluded that the introduction of BO in polymers P2 and P4 was the cause of the strong and broad absorptions observed in the UV–vis spectra. Furthermore, lower molecular orbital energy levels were achieved, including a 0.05–0.1 eV reduction in the band-gap and lower HOMO energies; for example, −5.33 and −5.36 eV for P1 and P3 and −5.39 and −5.53 eV for P2 and P4, respectively. Therefore, greater PCE values were obtained using the BO-containing polymers as the active layer in a conventional PV cell; namely, PCE was 1.2% for P2:$PC_{71}BM$ (1:4, 0.5 wt %).

Results and discussion

Synthesis and characterization of the polymers

Scheme 1 illustrates the chemical structure and synthesis of the monomers and polymers. The anthracene derivatives, which act as donors, 2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)anthracene (D1) and 2,2′-(9,10-bis(2-ethylhexyloxy)-9,10-dihydroanthracene-2,6-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (D2), which has a 2-ethylhexyloxy side chain at the 9- and 10-C positions of D1 (Scheme 1) were synthesized. Additionally, benzo-2,1,3-thiadiazole, 4,7-bis(5-bromothiophene-2-yl)-5,6-bis(octyloxy)-benzo-2,1,3-thiadiazole (A1), which is a benzo[-*c*][1,2,5]oxadiazole derivative, and 4,7-bis(5-bromothiophen-2-yl)-5,6-bis(octyloxy)benzo[*c*][1,2,5]oxadiazole (A2) were prepared. Using these donors (D1 and D2) and acceptors (A1, A2), the D–A type polymers poly[2,6-anthracene-*alt*-4,7-bis(thiophen-2-yl)-5,6-bis(octyloxy)benzo[*c*][1,2,5]thiadiazole] (P1), poly[2,6-anthracene-*alt*-4,7-bis(thiophen-2-yl)-5,6-bis(octyloxy)benzo[*c*][1,2,5]oxadiazole] (P2), poly[9,10-bis(2-ethylhexyloxy)anthracene-*alt*-4,7-bis(thiophen-2-yl)-5,6-bis(octyloxy)benzo[*c*][1,2,5]thiadiazole] (P3), and poly[9,10-bis(2-ethylhexyloxy)anthracene-*alt*-4,7-bis(thiophen-2-yl)-5,6-bis(octyloxy)benzo[*c*][1,2,5]oxadiazole] (P4) were prepared by using the Suzuki coupling reaction. The polymerization reaction was performed in toluene in the presence of $Pd(0)(PPh_3)_4$ catalyst, 2 M aqueous potassium carbonate as the base, and Aliquat 336 as a surfactant for 48 h at 90–95 °C. After completion of the polymerization, an end-capping reaction was conducted by adding bromobenzene and phenylboronic acid and stirring the solution for 3 h. The obtained powders were re-precipitated in methanol and purified by Soxhlet extraction using methanol, acetone, chloroform, and *o*-dichlorobenzene, in that order. Finally, the *o*-dichlorobenzene fraction was re-precipitated in methanol. The obtained powders were dark purple solids. P1, P2, P3, and P4 had isolated yields of 29, 59, 82, and 59%, respectively. Polymer P1 had low solubility in *o*-dichlorobenzene and, even at elevated temperatures, only partially dissolved. In contrast, P2 was mostly soluble in *o*-dichlorobenzene. Both P3 and P4 showed good solubility in general organic solvents such as chloroform ($CHCl_3$), tetrahydrofuran (THF), chlorobenzene, and *o*-dichlorobenzene. The synthesized polymer structures were further analyzed by ^1H NMR and elemental analysis (EA) (see in ESI, Fig. S1).

Table 1 summarizes the molecular weights and thermal properties of the polymers. Number average molecular weights (M_n) were determined using gel permeation chromatography with polystyrene as the standard and were 15, 13, 21, and 23 kDa with narrow PDI distributions of 1.6, 1.5, 1.9, and 1.3 for polymers P1–P4, respectively. Using thermogravimetric analysis (TGA), P1–P4 we were shown to have high thermal stability, even between 250 and 290 °C where they showed 5 wt% loss. These results imply that the synthesized polymers could be used in polymeric solar cells or other optoelectronic devices, as shown in Fig. S2.

Optical properties

The UV–vis spectra of the polymers in the solution phase (Fig. 1(a)) and film-phase (Fig. 1(b)) are shown in Fig. 1, with a summary in Table 2.

As shown in Fig. 1, all polymers have two absorption peaks in the range of 300 to 800 nm. The absorption peaks that appear at high-energy wavelengths (ca. 349–356 nm) are due to π–π^* transitions. In contrast, the absorption peaks at lower energy wavelengths (ca. 505–548 nm) are due to the intramolecular charge transfer (ICT) between the donors and acceptors [32,33].

In solution (*o*-dichlorobenzene), polymers P1 and P2 have similar absorption peaks with pairs of peaks was observed at 349 and 541 nm for P1 and 350 and 548 nm for P2. On the other hand, in solution, P3 and P4, which both have a 2-ethylhexyloxy side chains, the absorption peaks were blue-shifted with respect to P1 and P2 at 348 and 505 nm for P3 and 356 and 507 nm for P4. The maximum absorption wavelengths of the thin films (λ_{max}) were red-shifted by 1–48 nm compared to the solution state UV–vis spectra. This implies that in the film state there are stronger intermolecular interactions between the polymer chains than the solution state, leading to efficient 2-D stacking [34]. In particular, for P1 and P2, the absorption peaks located at about 600 nm have shoulders that arise due to their ordered solid-state structures. This phenomenon indicates that the polymers not only effectively reduce the steric hindrance in the solid state, but they also promote stronger chain stacking, even in solution [35]. Moreover, in the film state, the polymers have λ_{max} at 363 and 596 nm for P2 and 357 nm and 547 nm for P4, and these values are red-shifted (Δ = 1–48 nm) compared to those of polymers P1 and P3. For BO-containing polymers, better absorption intensity at longer wavelengths was observed compared to the BT-containing polymers. This is due to the greater electronegativity of oxygen than sulfur, which increases ICT effect in BO-compared to BT-containing polymers [36]. The electron configuration of oxygen and sulfur are $1s^2/2s^2/2p^4$ and $1s^2/2s^2/2p^6/3s^2/3p^4$, respectively. The nucleus of oxygen can affect the neighboring electrons and exerts a large force on the peripheral electron because an oxygen atom is smaller than a sulfur atom [37]. The calculated band-gaps of P1–P4 were calculated from the UV onset values and are 1.91, 1.86, 1.93, and 1.83 eV, respectively. The BO-containing polymers P2 and P4 have smaller band-gaps than either P1 or P3 [26].

Orientation analysis

The spacer structure of the polymers and the ordering and crystallinity of the thin films were analyzed by X-ray diffraction at annealing temperatures.